Old Dominion University Research Foundation

DEPARTMENT OF MECHANICAL ENGINEERING & MECHANICS
COLLEGE OF ENGINEERING & TECHNOLOGY
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA 23529

MORPHOLOGY AND MICROSTRUCTURE OF COMPOSITE MATERIALS

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and

S. N. Tiwari, Principal Investigator

Progress Report
For the period ended June 30, 1991

Prepared for
National Aeronautics and Space Administration
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Under
Research Grant NAG-1-569
Robert M. Baucom, Technical Monitor
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FOREWORD

This is a progress report on the research project, "Chemoviscosity Modeling for Thermosetting Resins," for the period ended June 30, 1991. Special attention during this period was directed to the study of "Morphology and Microstructure of Composite Materials." The work was supported by the NASA Langley Research Center (Polymeric Materials Branch of the Materials Division), research grant NAG-1-569. The grant was monitored by Mr. Robert M. Baucom.

MORPHOLOGY AND MICROSTRUCTURE OF COMPOSITE MATERIALS

K. SRINIVASAN[1] AND S. N. TIWARI[2]

ABSTRACT

Lightweight continous carbon fiber based polymeric composites are currently enjoying increasing acceptance as structural materials capable of replacing metals and alloys in load bearing applications. As with most new materials, these composites are undergoing trials with several competing processing techniques aimed at cost effectively producing void free consolidations with good mechanical properties. As metallic materials have been in use for several centuries, a considerable database exists on their morphology / microstructure; and the interrelationships between structure and properties have been well documented. Numerous studies on composites have established the crucial relationship between microstructure / morphology and properties. This report seeks to document the various microstructural and morphological features of composite materials, particularly those accompanying different processing routes.

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1 Research Associate, Department of Mechanical Engineering and Mechanics, Old Dominion University, Norfolk, VA 23529-0247.

2 Eminent Professor, Department of Mechanical Engineering and Mechanics, Old Dominion University, Norfolk, VA 23529-0247

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1. INTRODUCTION

Resins utilized for composites fall into two classes: thermoplastic and thermoset. Early on in the development of composites, thermoset resins were used exclusively. A vast number of processing techniques were developed for such materials. The key attributes of thermosets that shaped early processing routes for composites were low viscosities, ability of monomeric species to react and produce highly crosslinked polymers, limited shelf stability and solubility of the monomeric species in a wide variety of cheap and safe solvents. The most commonly adopted procedure for putting together thermosetting resins and fibers was solution prepregging. However, a number of deficiencies were later identified with the first generation thermosets that prevented the widespread acceptance of these materials. Chief among these were brittleness, limited shelf life, long and complex cure cycles and a propensity for moisture absorption. Thus thermoplastic materials were proposed as alternative matrices for composites.

Unlike thermosets, thermoplastic materials were synthesized to a desired high molecular weight and then combined with fibers, so the processing operation was merely one of consolidation, with no further chemical reaction occuring during the formation of a part. Thus, in addition to imparting toughness, moisture resistance and repairability, fast processing cycles with thermoplastics could potentially provide higher rates of production. The high molecular weights of the starting polymeric material however greatly increased both melt temperatures and viscosities and made difficult the production of good quality void-free laminates. Further, in order to reduce the succeptibility of these materials to common aerospace solvents, these materials were engineered by molecular structure to be insoluble in most common solvents. Hence until recently, melt impregnation has been the most favored route for producing prepregs of thermoplastic materials.

Several other techniques are currently under consideration for both thermoplastics and thermosets, and these include pultrusion, powder coating, resin transfer molding, film stacking and comingling. More recently, the traditional lines between thermosetting and thermoplastic composites has been considerably blurred, as

researchers have attempted to combine favorable elements of both in complex resin formulations. Typically these are multi-phase, multi-component systems engineered to provide a specific set of properties aimed at specific end applications. Quite expectedly, these materials possess complex and processing dependent microstructures.

2.0 CLASSIFICATION AND CHARACTERIZATION

Microstructural / morphological details have been shown to be key determinants of composite properties [1]. More importantly, the quality of the final laminated structure is seen to be highly dependent on the quality of the starting prepreg / towpreg material. This is because copious flow needed to fill extensive dry regions in the lamina, frequently produces fiber architectural distortions that are detrimental to laminate level properties. Further, an important requirement for any part or structure made of composites is reliability. This requires uniform quality levels and adherence to precise forming operations, which can only be engendered through careful control of microstructure and morphology.

For studying the microstructural details, several arbitrary classification schemes for composite materials can be devised. These include type of material, method of production, layup details and structure considerations. Typical techniques used to observe composite microstructures include optical microscopy, scanning electron microscopy and radiographic and ultrasonic techniques. Often indirect supporting evidence is also obtained from physical characterization techniques such as thermal and mechanical tests.

Single component systems can show either semi-crystalline or amorphous morphology. All thermoset systems are necessarily amorphous as are a vast majority of thermoplastic systems. A molecular description of the polymer characteristics of such systems requires a probe of the order of a few Angstroms, which is inaccessible except in some of the latest sophisticated Scanning - Tunneling systems. However optical microscopy in such composite systems can still reveal gross features such as resin and fiber distribution, fiberwash, curing agent particles, voids and inter and intralaminar cracks. For *eg.* Fig 1 depicts an optical micrograph of a PMR-15/IM-7 composite (a highly crosslinked system). Numerous voids and interply cracks are visible possibly due to improper formulation and / or processing and thermal stresses during cooldown. Certain thermoplastic systems possess semi-crystalline morphology. These systems reveal fine texture details in either polarized light microscopy or electron microscopy. Figure 2 is an SEM photomicrograph of the spherulitic texture seen in a

PEEK/AS-4 specimen. Numerous fine spherulites (typically 2 - 3 microns in diameter) are visible growing outward from several point sources and impinging to produce the semi-crystalline texture. It is worth noting that observation of this spherulitic crystallinity is strongly dependent on the angle of the incident beam.

In recent times, in response to a demand for toughened composite systems, researchers have developed Interpenetrating Polymer Network systems (IPNs) and semi-IPNs. Following accepted nomenclature in the composite community, IPNs consist of two (or more) crosslinked systems cured *insitu*, such that the networks of both materials are closely intertwined on a molecular scale. Semi-IPNs are created when a thermosetting resin cures in the presence of a high molecular weight thermoplastic system. As these mixtures take place on a molecular level, the fine microstructural features are indistinguishable by common optical or electron microscopic techniques. Information is obtained on such systems by indirect techniques, such as mechanical or thermal probes. In such mixed systems phase separation may or may not occur. When phase separation does not occur, such systems are termed co-continous (for *eg.* the 977-2 system). When phase separation does occur, the minor phase may segregate to form discrete particles in the major phase (as is common with most rubber modified epoxies), or phase inverted (the major phase may form discrete particles in the minor phase) microstructures may manifest themselves (as in the case of 8551-7).

Yet another approach for toughening composites is interleafing. Here a thin layer of a tough polymer is placed at ply interfaces to blunt cracks and provide ductility. Figure 3 (taken from Reference 2), shows a schematic of such an interleaved 1808-I system, where the prepreg has a coating of a thin, tough polymer film on one surface. Particles that coalesce into films during consolidation have also been employed for interleaving brittle composites; Fig. 4 shows an electron micrograph of an RP46-5218/IM-7 system. Here the interleaf material (Matrimid 5218) is dispersed in the form of a fine powder on a solution impregnated RP46 system. During consolidation, the powder melts and coalesces to form the desired interfacial film. As mentioned earlier, the quality of the laminate is crucially dependent on the quality of the prepreg / towpreg. This naturally leads into a discussion of the different processing

techniques that combine resins and fibers to form prepregs / towpregs and the morphologies that result.

Drum winding, a laboratory scale variant of solution prepregging, is typically a batch process. Here fibers are led into a bath of resin solution and the impregnated tow is wound around a rotating mandrel in overlapping fashion to yield a continous prepreg sheet. The operation depends on several key processing parameters, such as solids concentration of the bath, the resins pickup, the spreading of the fiber tow in the bath, the rotational speed of the drum and the degree of overlap among sequential tow layups. Detailed mention is made of this process in Reference 3. While the process yields good quality prepreg for experimental evaluation of new resin systems, it suffers from some notable deficiencies. One key requirement is the ability of the resin to be solvated by a cheap, non-toxic solvent. Further, as the prepreg is wound on the drum with some tension, the resin preferentially migrates to the outside of the drum. This distorts the morphology and leads to resin-rich and resin-poor surfaces. Figure 5 shows an electron micrograph of the back side (the side next to the drum surface), in a Polyimidesulfone/AS-4 prepreg. Note the resin poor surface and the overlap of the tows to form the prepreg. Naturally, such a prepreg system when consolidated, shows heterogeneous resin distribution and may provide for preferential paths for subsequent laminate failure, particularly if resin poor interfaces are adjacent.

For resin systems that cannot be easily solvated by common solvents, process technologies that rely on melt impregnation have been employed. Two such processes are most common : melt impregnation and pultrusion. Both rely on passing the fibers through a bed of molten resin. Here the key parameters are thermal stability of the resin and resin viscosity. Pultrusion is also feasible with powder impregnated tows (to be discussed later). Both processes involve operational difficulties and considerable care and control of processing conditions must be exercised if good quality prepreg is to be obtained. Figures 6 and 7 show prepreg morphologies of melt impregnated APC-2 (PEEK/IM-7) and pultruded Ultem 1000/AS-4 prepregs. Both are excellent quality prepregs and lend themselves to easy void-free consolidations in complex, multi-angle thick layups. Note that the resin in both forms a smooth coating over individual fibers leading to an excellent fiber-resin interface. However

considerable process standardization is required before acceptable quality preforms are generated from both processes. Figures 8 and 9 reveal this fact. Figure 8 is an example of LaRC TPI 1500/T300 melt prepreg from Mitsui. As is evident from the figure, the resin has not been able to penetrate the fiber tows, leading to many bare fiber regions. The individual tows too have not been enmeshed properly. Consequently, such a prepreg system does not consolidate to produce good quality laminates (as determined by C-Scans), even at very high consolidation pressures. Figure 9 likewise, is a poorly pultruded Polyimidesulfone/AS-4 prepreg that did not provide good quality laminates.

In order to avoid solvent handling (as with solution prepregging) and working with high temperature melts, powder towpregging has been suggested as a cost-effective alternative (4) method of bring fibers and resins together. Figures 10 and 11 show powder coated tows of LaRC TPI/AS-4. In this process, the fiber tows are led into a chamber of fine agitated resin powder, which is then sintered onto the fiber by passing through a hot zone. As Fig. 10 shows, uniform deposition of the powder particles is possible by this process. Further good quality laminates can be produced from such coated tows. An important parameter that must be controlled is the particle size. However as Fig 11 shows, the unprotected fiber may undergo some abrasion during the process.

A variant of the powder process involves co-extrusion of an onion skin around a tow to produce a Fiber Impregnated Tow (FIT). This process has recently been suggested as an effective towpregging technique for thermoplastic resins. Figures 12 through 15 show the microstructures of PEEK/AS-4 and Ultem 1000/AS-4 FIT materials. While the Ultem 1000 FIT shows good retention of the core powder, the PEEK FIT does not. Mechanical and processing data is lacking about this type of towpreg.

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3. Clarence E. Stanfield and Maywood L. Wilson, "Apparatus for Impregnation of Weak Fibers", NASA Tech Briefs, May 1986, p 46.

4. Robert M. Baucomb and Joseph M. Marchello, "LaRC Dry Powder Towpreg System", NASA TM 102648, April 1990.

Fig. 1 : PMR-15/IM-7 Composite Optical Micrograph

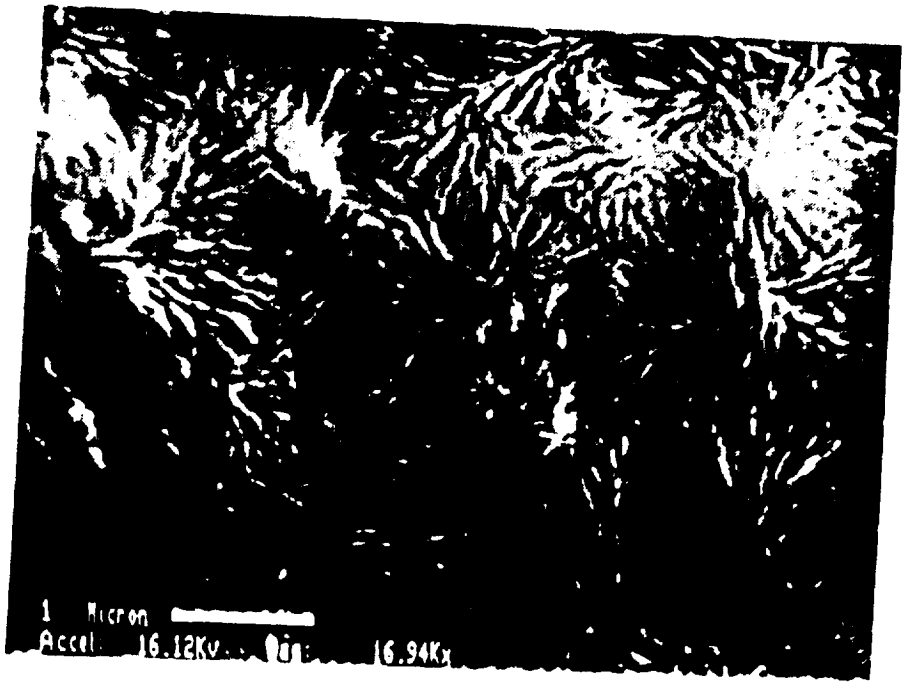

Fig. 2 : Spherulitic Morphology in PEEK/AS-4 Composite

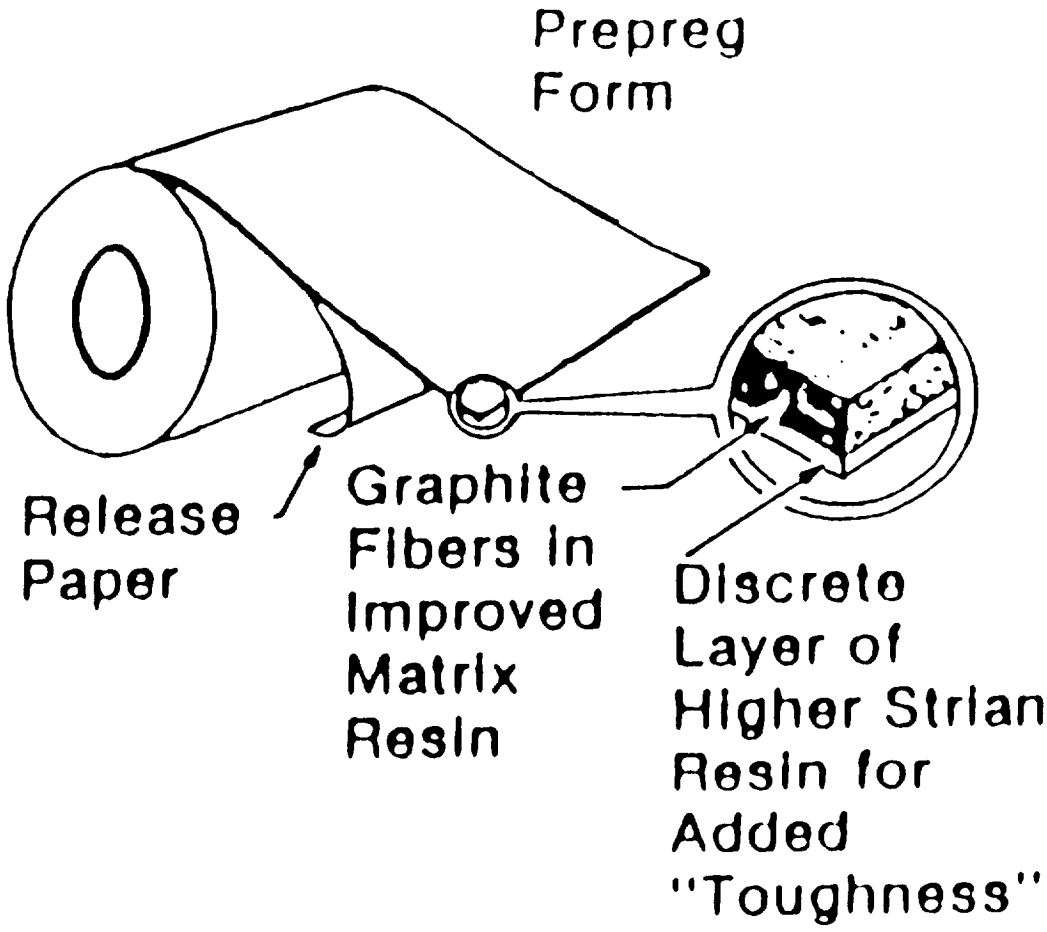

Fig. 3 : Schematic of Interleaved Prepreg System

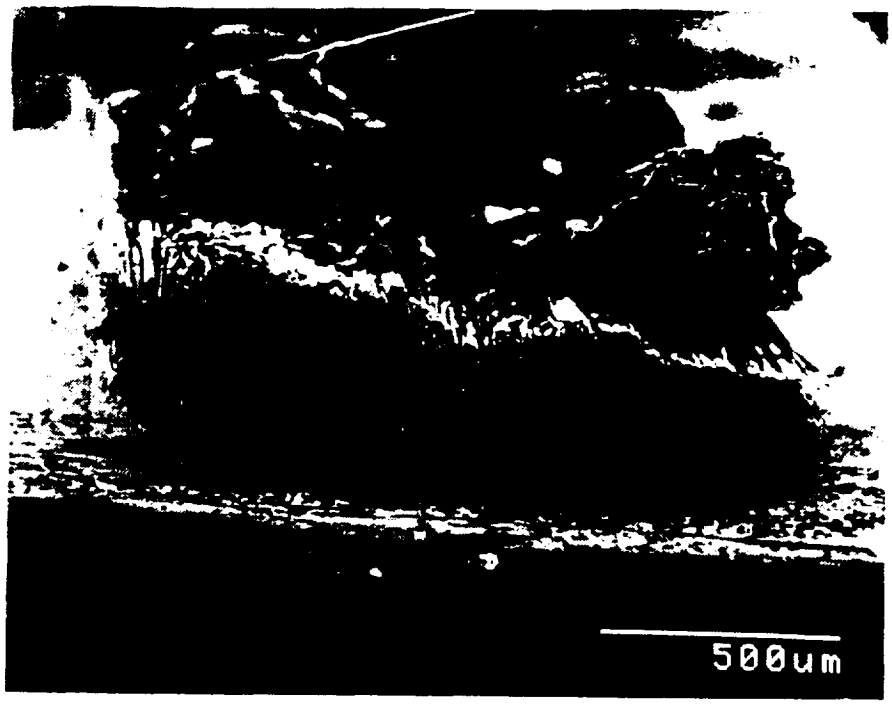

Fig. 4 : RP46-5218/IM-7 Interleaved Prepreg Micrograph

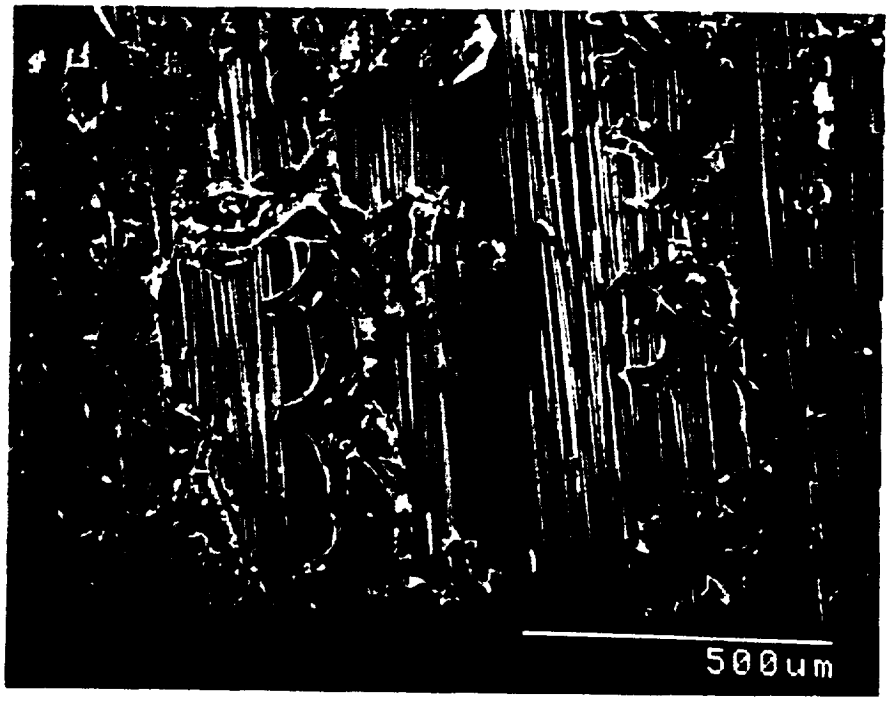

Fig. 5 : Polyimidesulfone/AS-4 Drumwound Prepreg Micrograph

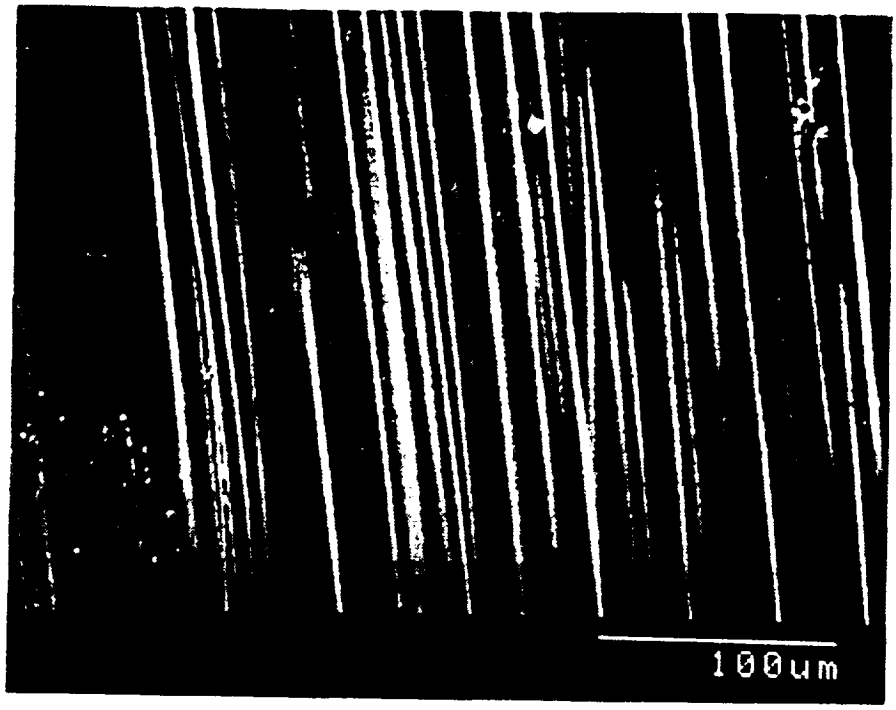

Fig. 6 : Melt Impregnated PEEK/IM-7 Prepreg

Fig. 7 : Pultruded U1000/AS-4 Prepreg

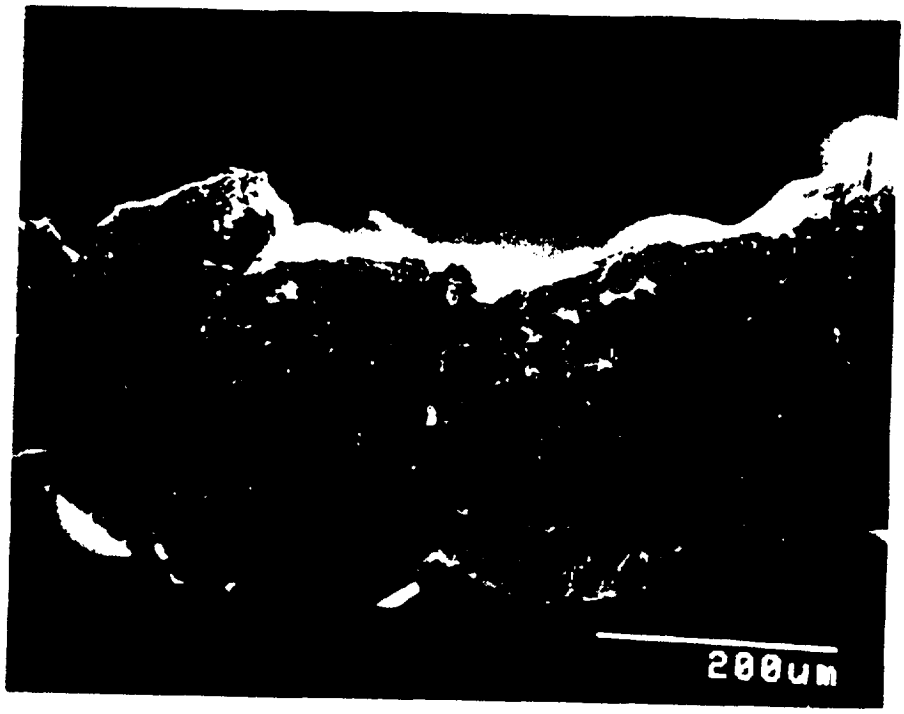

Fig. 8 : Melt Impregnated LaRC TPI 1500/T300 Prepreg

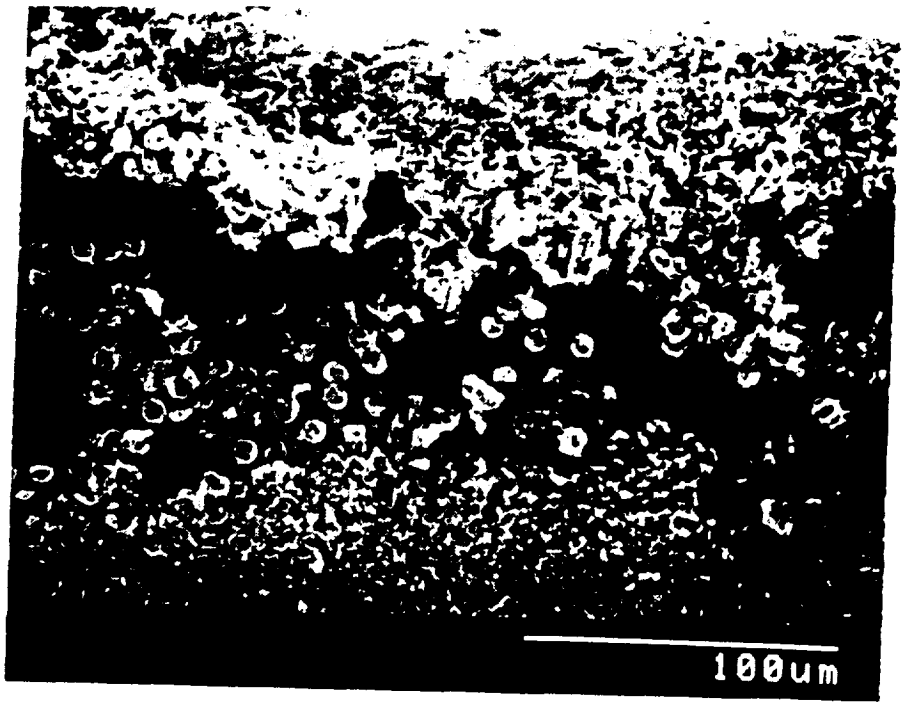

Fig. 9 : Pultruded Polyimidesulfone/AS-4 Prepreg

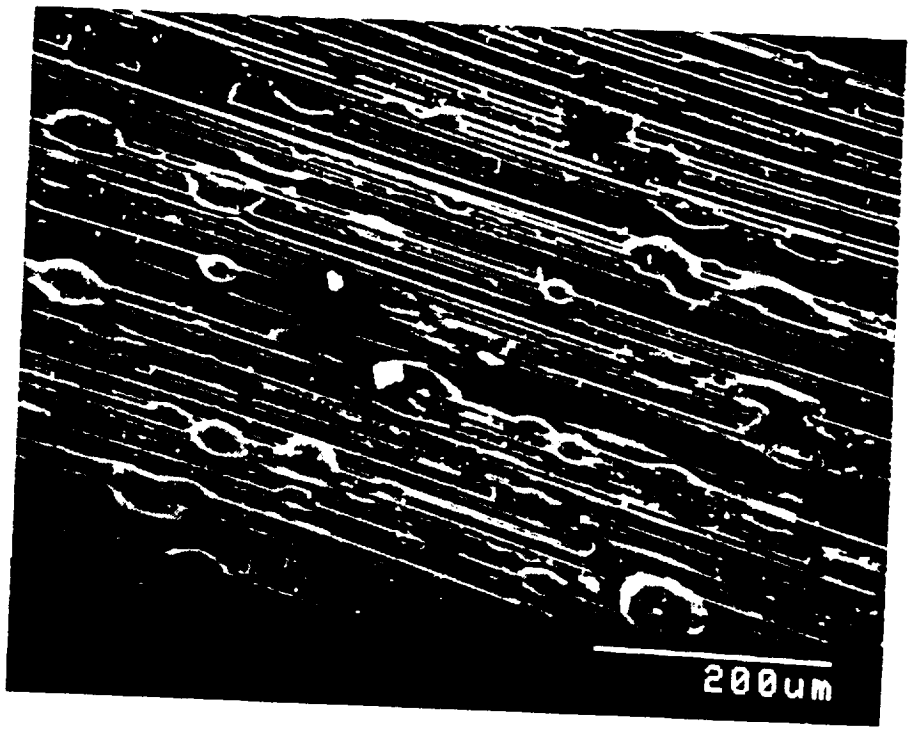

Fig. 10 : LaRC TPI/AS-4 Powder Coated Tow Morphology

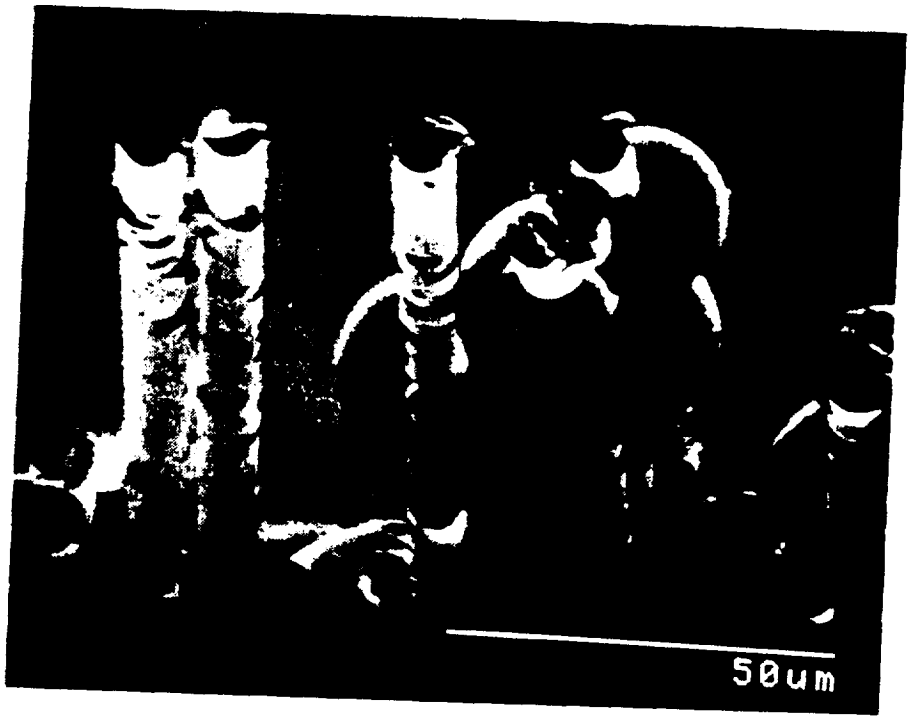

Fig. 11 : LaRC TPI/AS-4 Powder Coated Tow Morphology

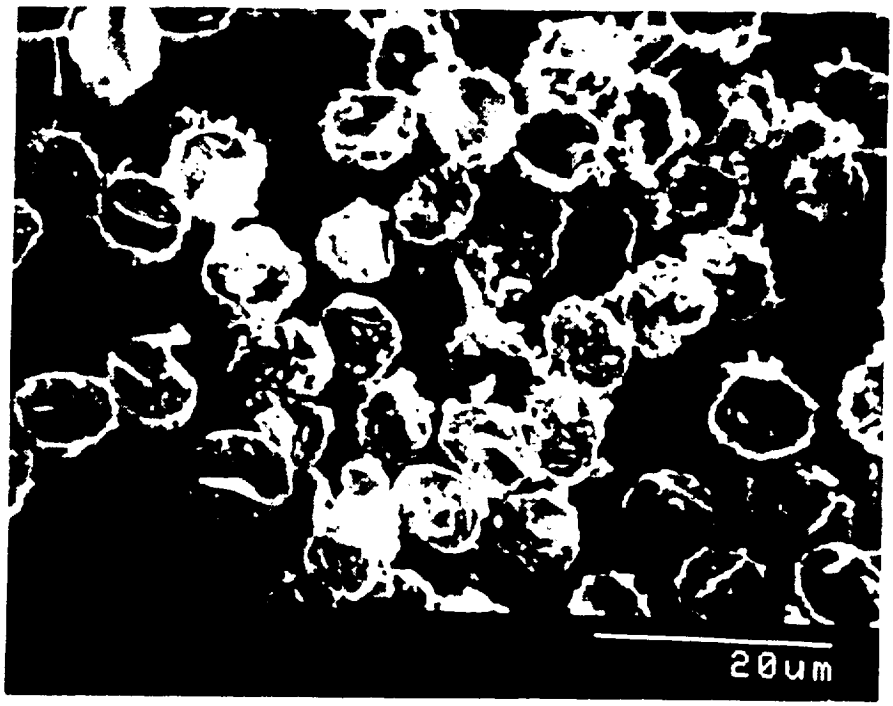

Fig. 12 : PEEK/AS-4 FIT Morphology

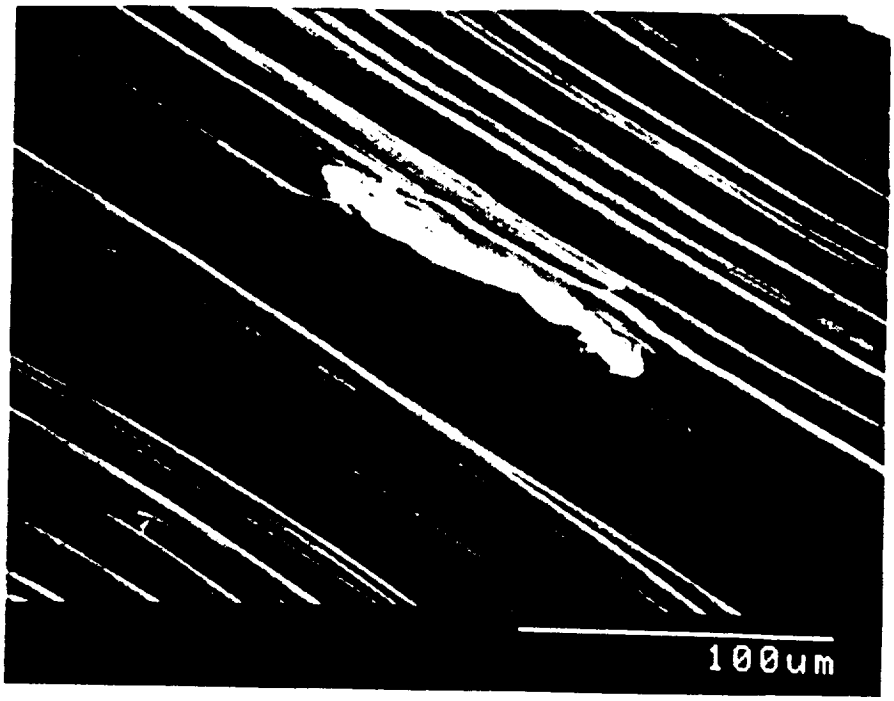

Fig. 13 : PEEK/AS-4 FIT Morphology

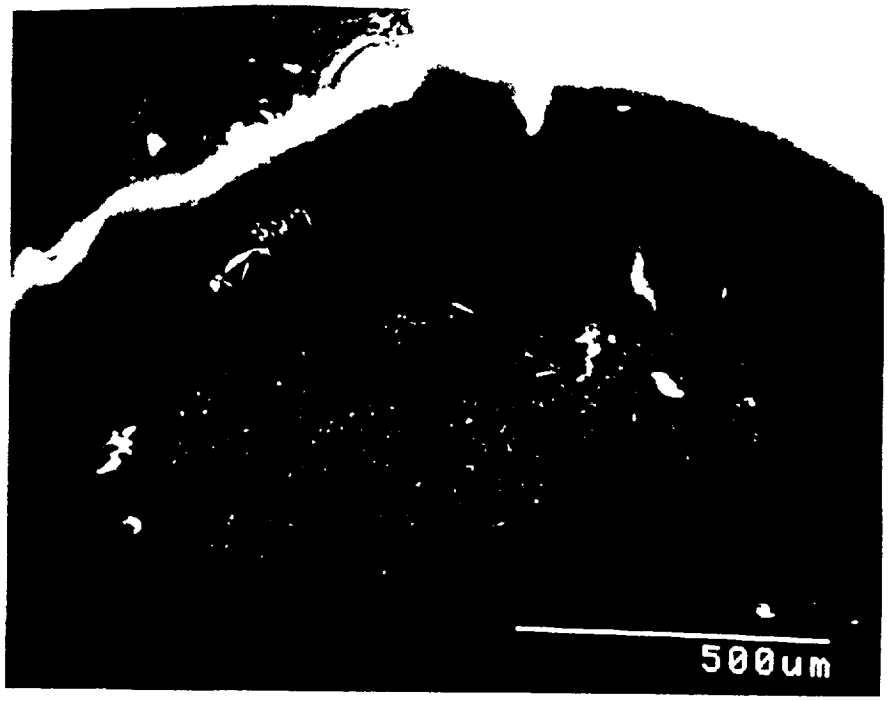

Fig. 14 : U1000/AS-4 FIT Morphology

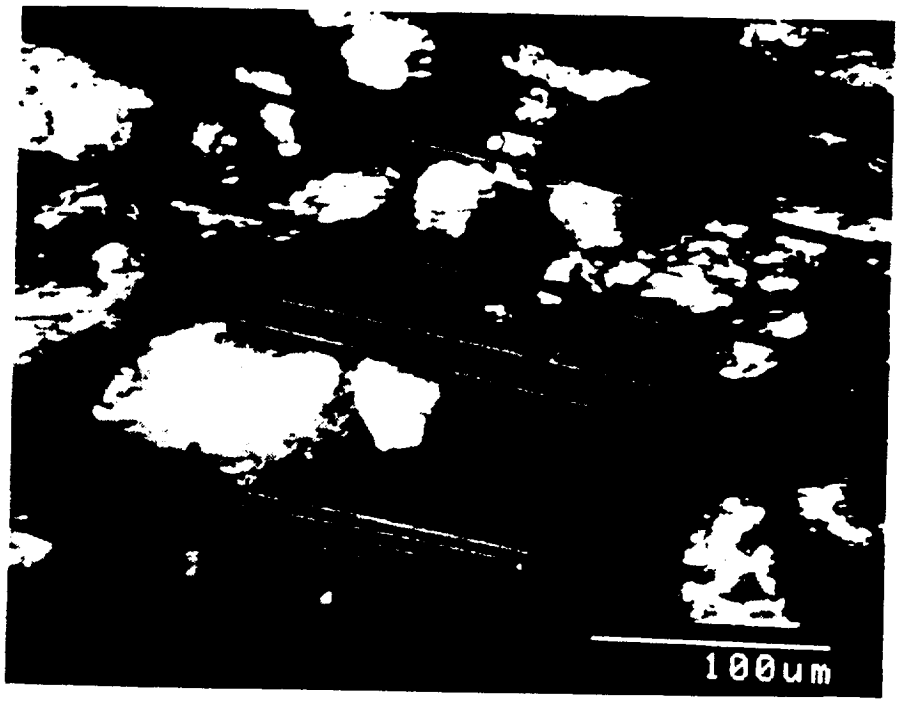

Fig. 15 : U1000/AS-4 FIT Morphology